OPTION A: ANALYTICAL CHEM
A4 – MASS SPECTROMETRY

IB Chemistry

TAD03

2.2.1 – Operation of Mass Spec

- 2.2.1 – Describe and explain the operation of a mass spectrometer
- What's it for? A **mass spectrometer** allows chemists to determine:
  - Relative atomic masses of atoms
  - Relative molecular masses of compounds
  - Structure of molecules
- How? By splitting up atoms, isotopes or molecules by their mass to charge ratio

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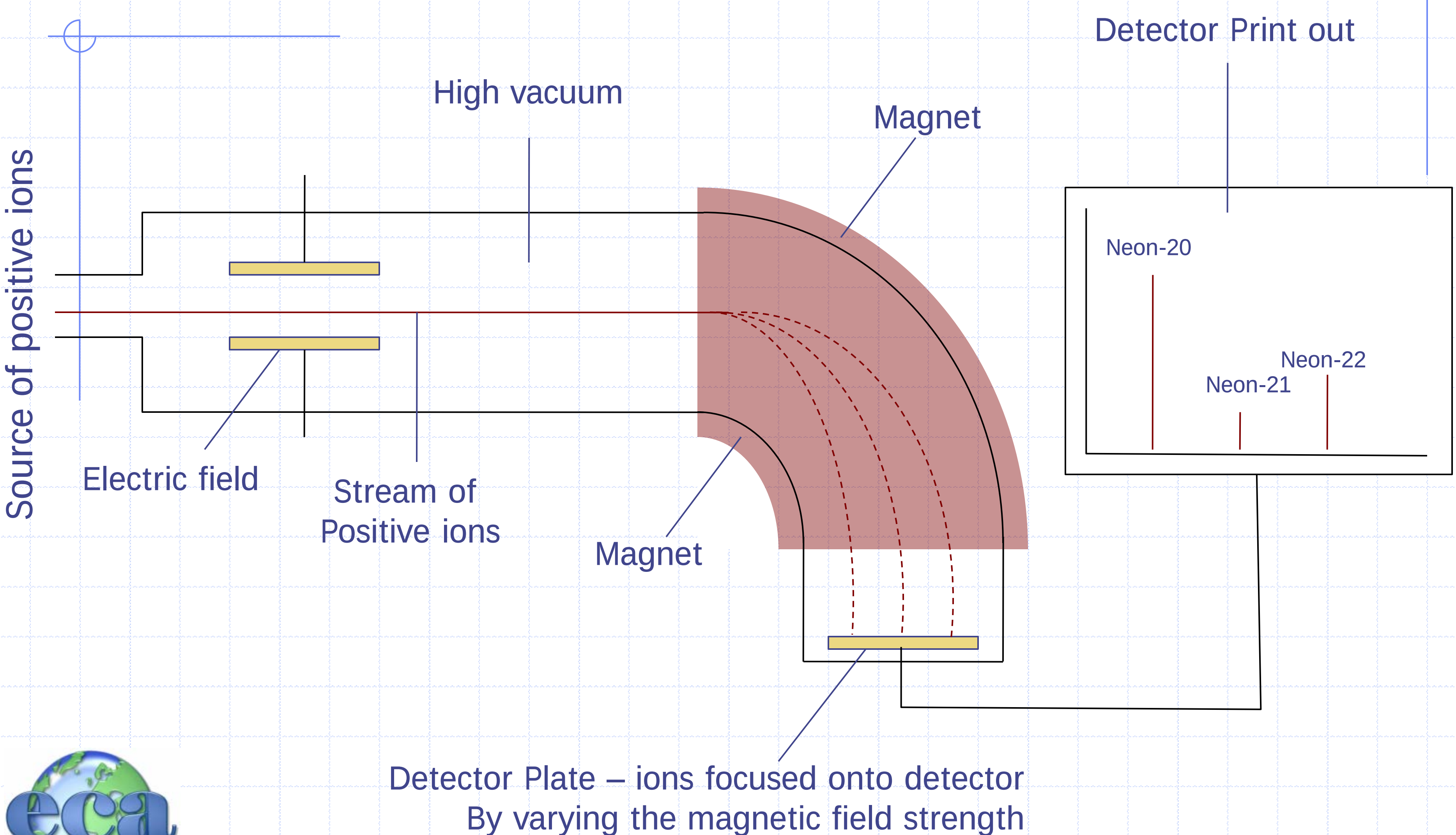
2.2.1 – Diagram of a Mass Spec



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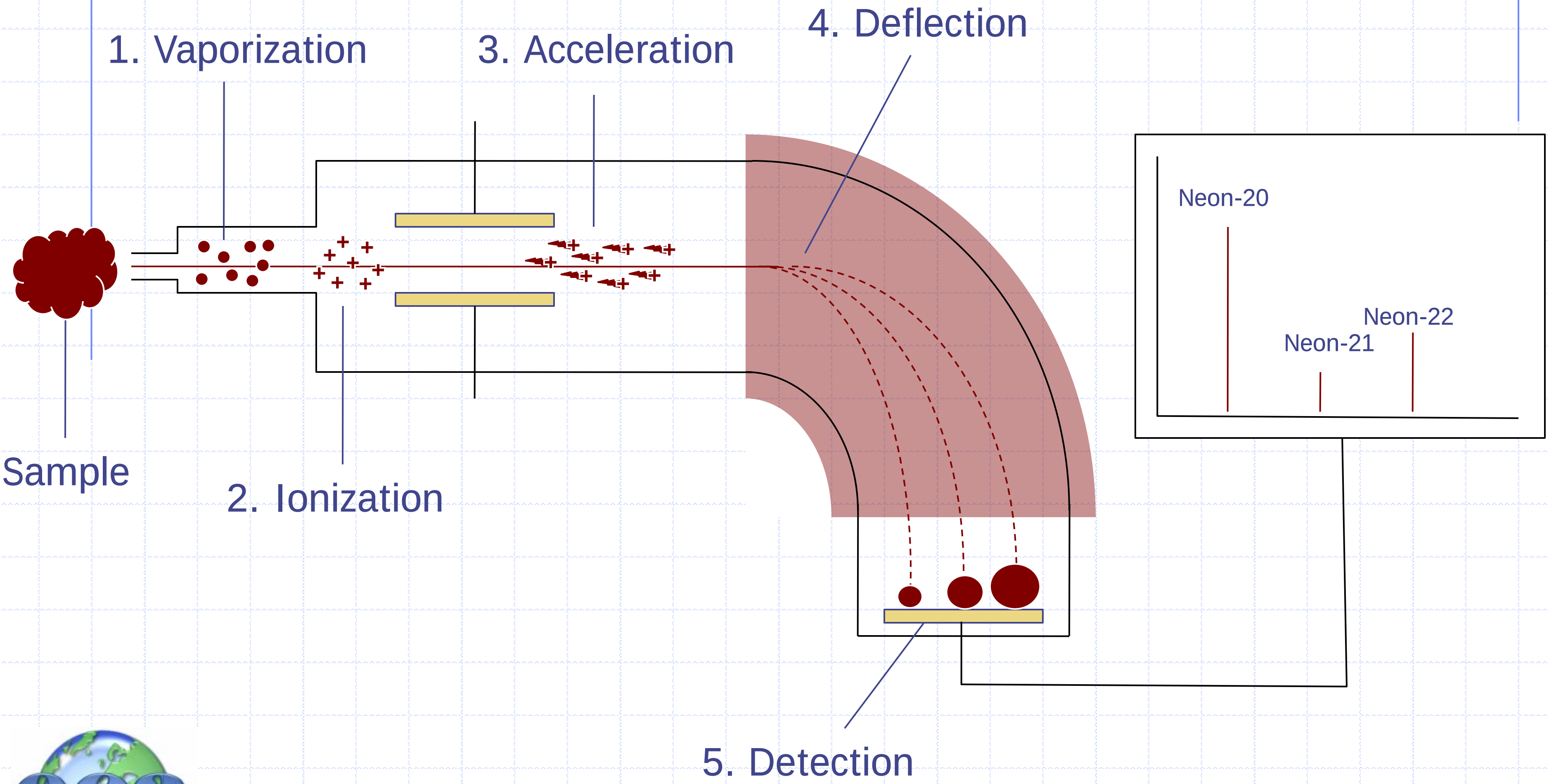
2.2.1 – Steps of a Mass Spec



2.2.1 – Explanation of MS steps

- **1. Vaporization**: sample is energized to the state of a gas
- **2. Ionization:** gas is bombarded with high-speed electrons, making uni-positive (+1 charge) ions
  - $M(g) + e^- \rightarrow M^+(g) + 2e^-$
  - All ions in the MS will have the same charge, diff mass
- **3. Acceleration:** the electric field accelerates the positive ions
- **4: Deflection:** a strong magnetic field deflects the particles based on their mass-to-charge (m/z) ratio
- **5: Detection:** a detector counts the numbers of each of the different ions that impact upon it, providing a measure of the percentage abundance of each isotope

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A4 – Mass Spectrometry

- A.4.1 Determine the molecular mass of a compound from the molecular ion peak. (3)
- A.4.2 Analyze fragmentation patterns in a mass spectrum to find the structure of a compound. (3) Examples of fragments should include:
  - $(M_r - 15)^+$ loss of CH_3
  - $(M_r - 17)^+$ loss of OH
  - $(M_r - 29)^+$ loss of C_2H_5 or CHO
  - $(M_r - 31)^+$ loss of CH_3O
  - $(M_r - 45)^+$ loss of COOH

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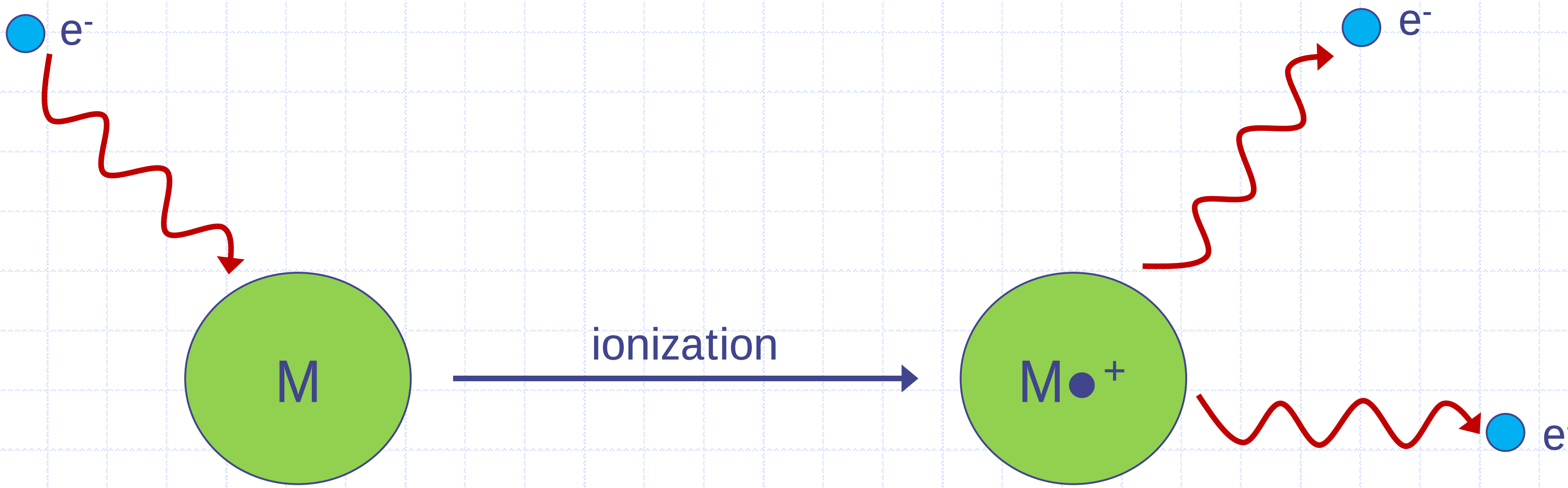
Molecular Mass Determination

A.4.1 Determine the molecular mass of a compound from the molecular ion peak. (3)

- Topic 2 was more about elements, their isotopes, and the elemental composition of compounds
- Option A is more about compounds and identifying their composition based on functional group behavior
  - If molecules are vaporized and subjected to the ionizing conditions inside a mass spectrometer, the mass-to-charge (m/e) ratio for the **molecular ion** can be measured, and hence the relative molecular mass (M_r) can be determined
  - The same simple steps of mass spec will apply

Ionization

- Bombarding molecules with high energy electrons (high KE) can ionize them by stripping off the outer electron leaving a cation with an unpaired electron (radical)

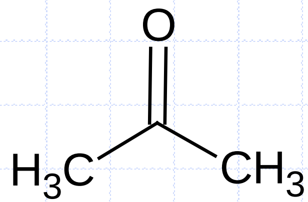


Molecule in sample

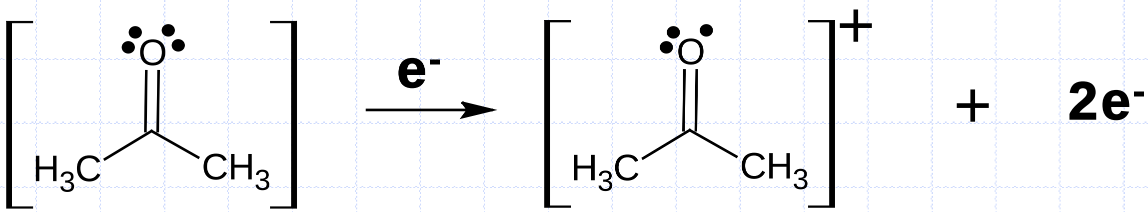
Cation with unpaired electron (radical cation)

Mass / Charge (m/e) Ratio

- A compound has a relative molecular mass (M_r)
  - Propanone: 58 g mol^{-1}



- The charge added to compounds will all the be same (generally uni-positive)
  - The ion formed is $CH_3COCH_3^+$



- Mass/Charge ratio = $\frac{58}{1} = 58$
  - As long as they are all uni-positive (control) – the mass is the only variable to be altered

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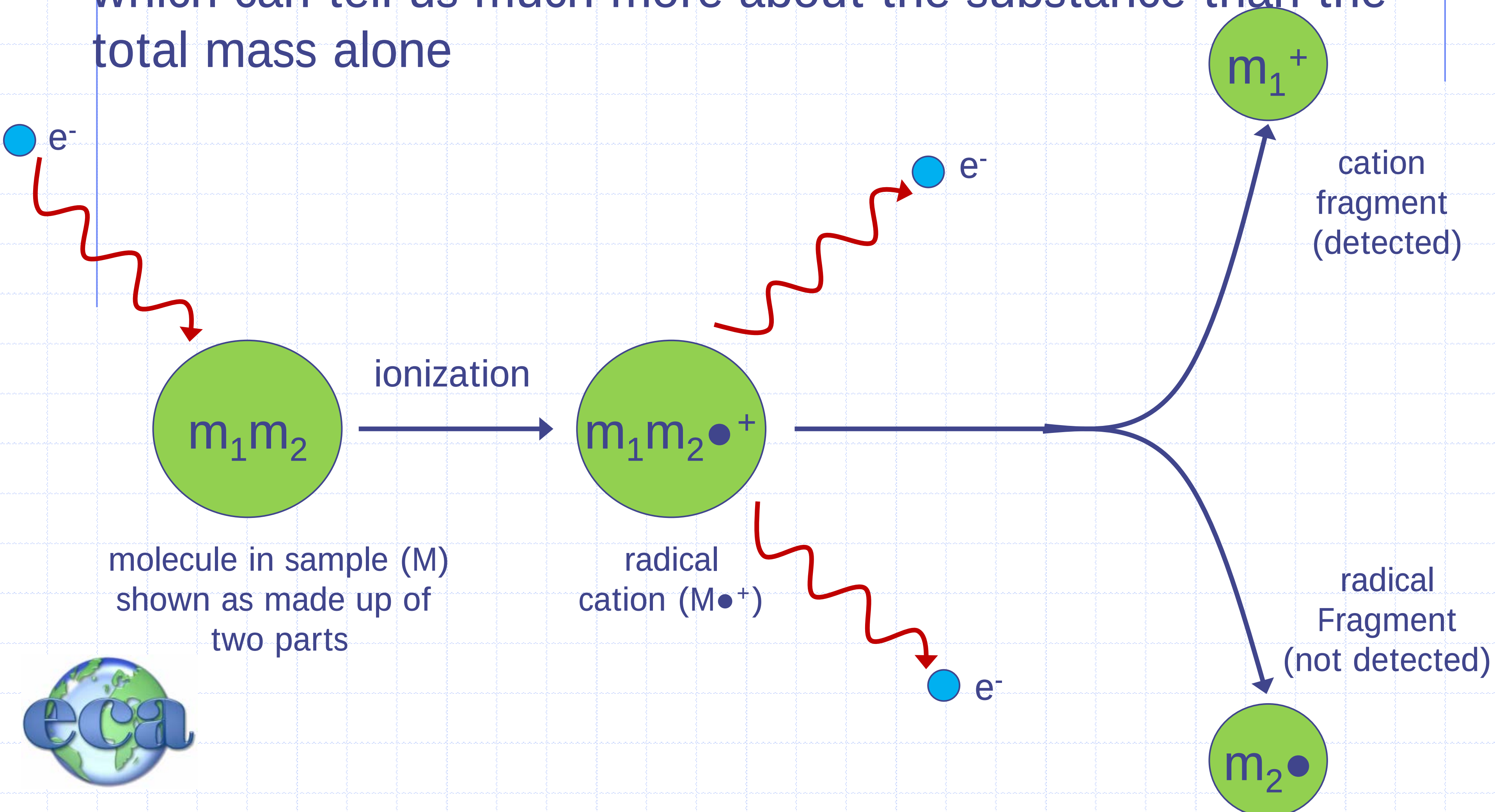
Molecular Fragments

- This bombardment also produces other compounds cations which can tell us much more about the substance than the total mass alone



Structure from Mass Spec

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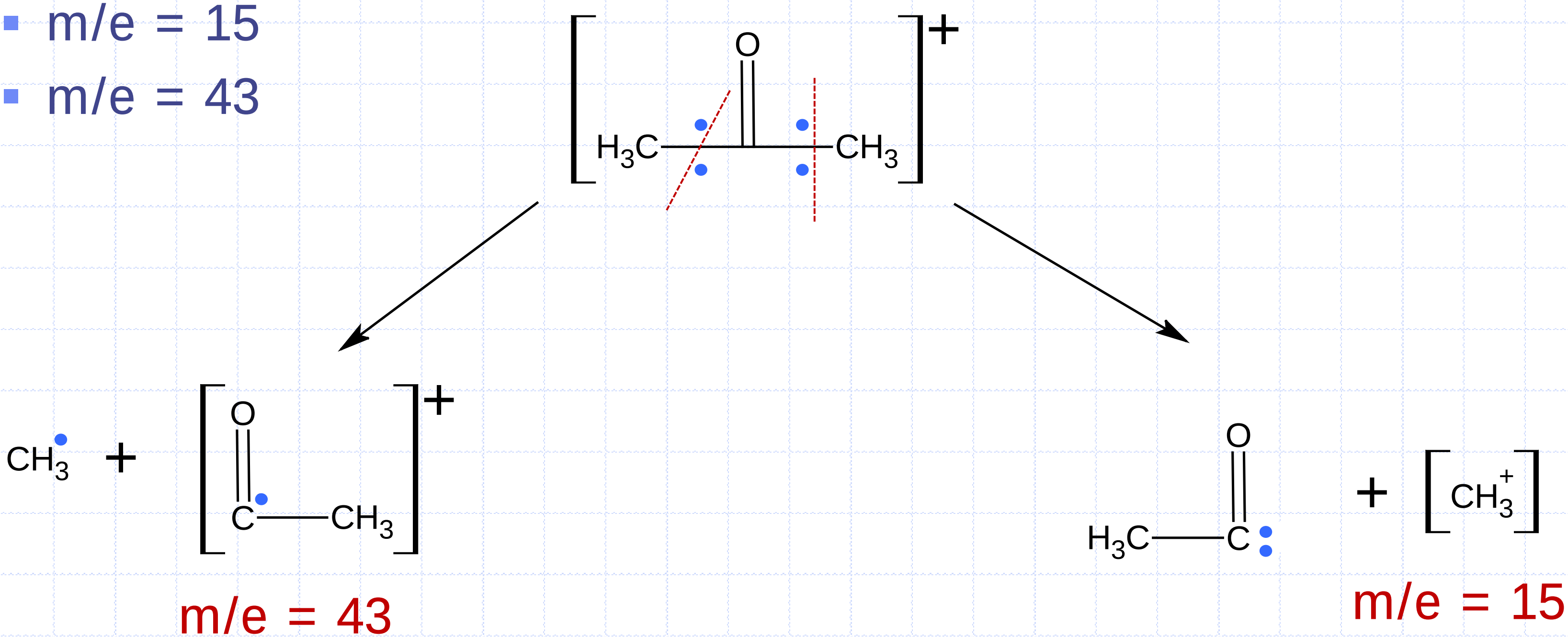
A.4.2 Analyze fragmentation patterns in a mass spectrum to find the structure of a compound. (3)

- If the ionizing electron beam in a mass spectrometer has sufficient kinetic energy, the molecular ions can undergo bond cleavage and **molecular fragments** are formed.
  - For Propanone, CH_3COCH_3, the peak at 58 will remain and new peaks at
    - m/e = 15
    - m/e = 43



Mass Spec Data

- For Propanone, the following peaks are seen

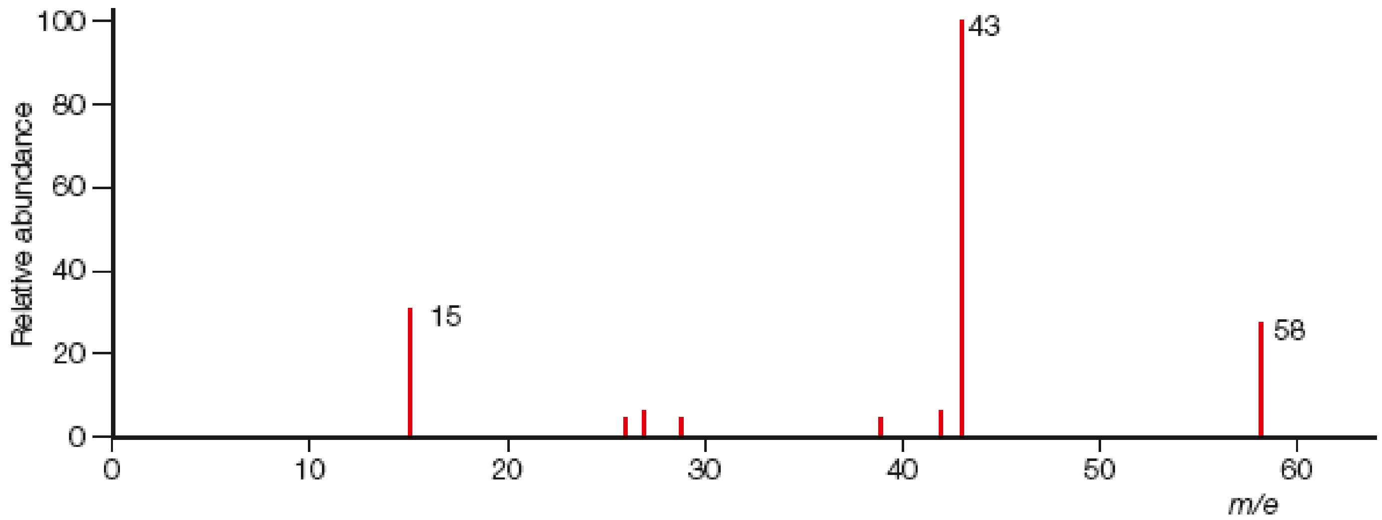


Figure 21.50 Mass spectrum of propanone

- In this last example it has been demonstrated that in order for mass spec to work, the molecular fragments must contain a charge (carbocations).
  - More stable fragments have larger peaks
  - Stability (from organic) = primary < secondary < tertiary

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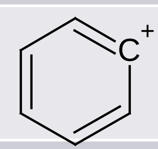
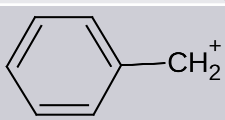
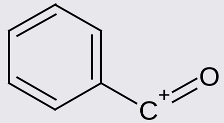
Common Molecular Fragments

Fragment	m/e	Structural formula
CH_3^+	15	$\overset{+}{C}H_3$
$CH_3CH_2^+$ or CH_2^+	29	$H_3C—\overset{+}{C}H_2$ $H\overset{+}{C}{=}O$
$CH_2NH_2^+$	30	$H_2\overset{+}{C}—NH_2$
CH_2OH^+	31	$H_2\overset{+}{C}—OH$
CH_3O^+ or $C_3H_7^+$	43	$H_3C—\overset{+}{C}{=}O$ $H_3C—CH_2—\overset{+}{C}H_2$
$CONH_2^+$	44	$O{=}\overset{+}{C}—NH_2$
$COOH^+$	45	$HO—\overset{+}{C}{=}O$
$C_6H_5^+$	77	
$C_6H_5CH_2^+$	91	
$C_6H_5CO^+$	105	

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Determine the Isomers of $C_2H_4O_2$

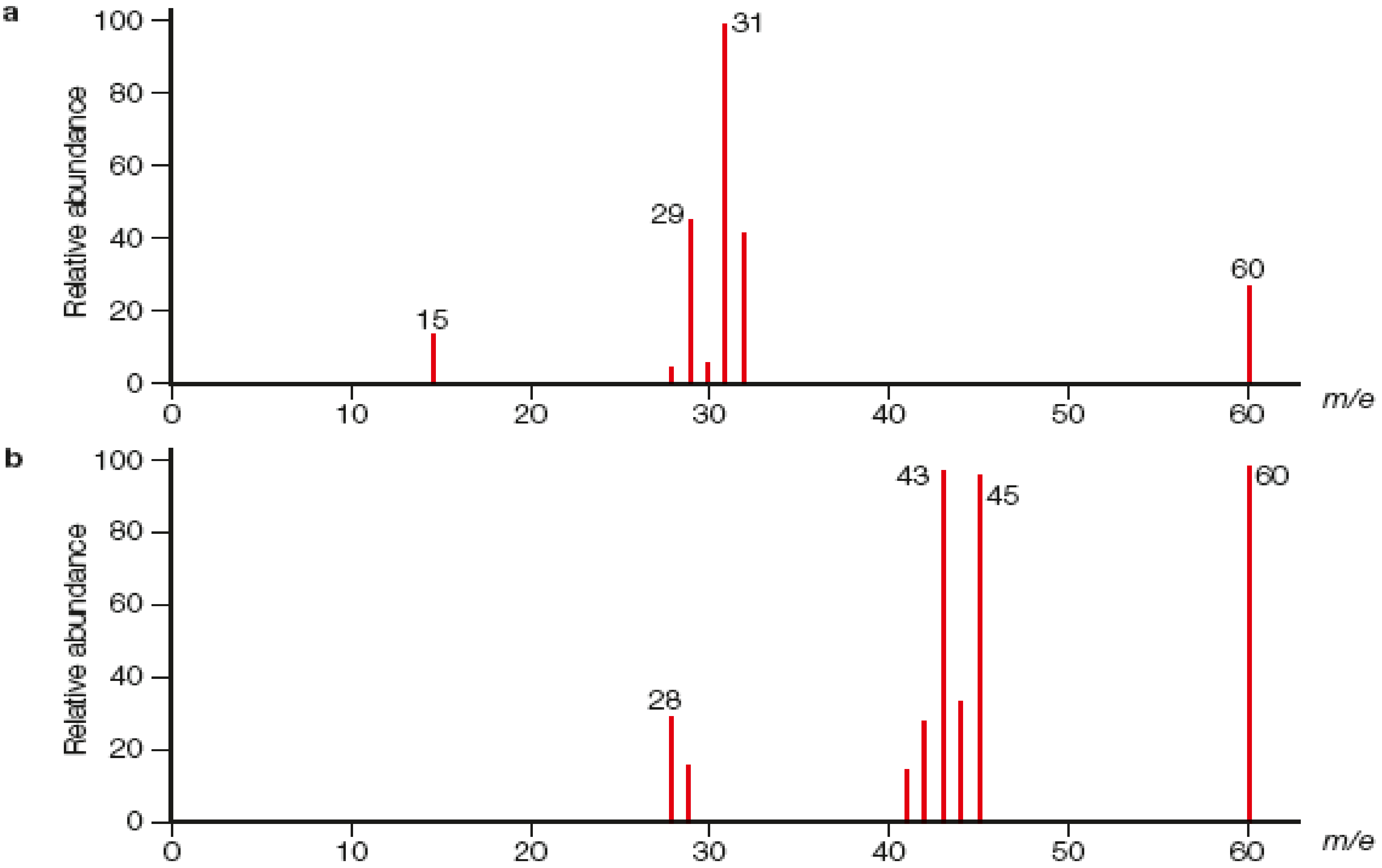

Figure 21.53 Mass spectra for $C_2H_4O_2$

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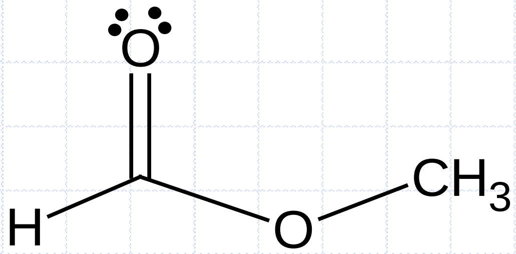
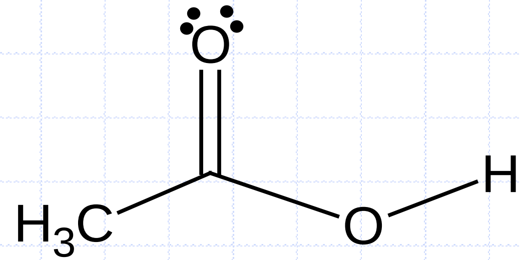
Reading Mass Spec Data

- Two isomers of $C_2H_4O_2$ (which were on your homework for A3) are:

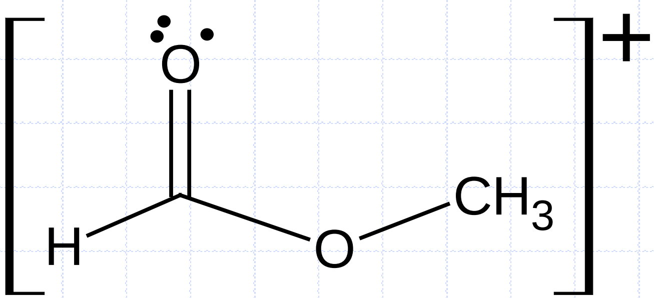


methyl methanoate

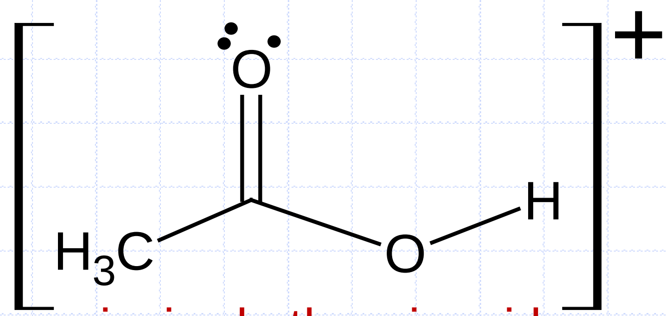


ethanoic acid

- Upon ionization, which electrons will most likely be stripped off?



ionized methyl methanoate



ionized ethanoic acid

- Now, we should be able to compare the mass spec data to the common fragments and identify each compound

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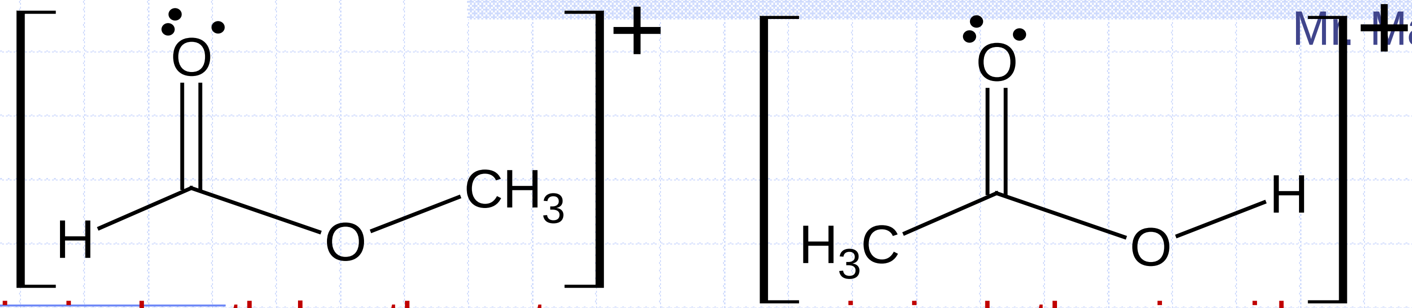

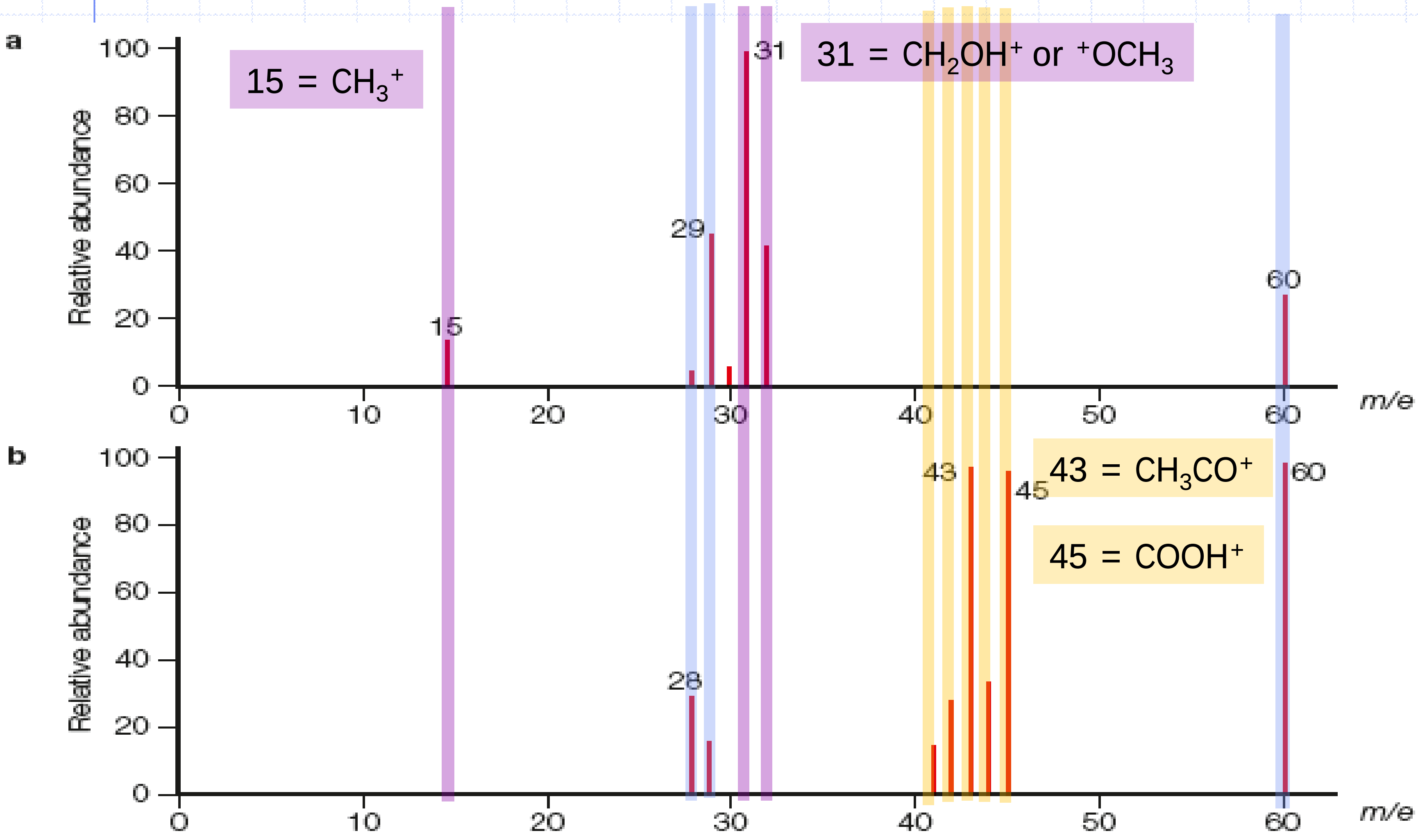

Figure 21.53 Mass spectra for $C_2H_4O_2$

Cleavage Points

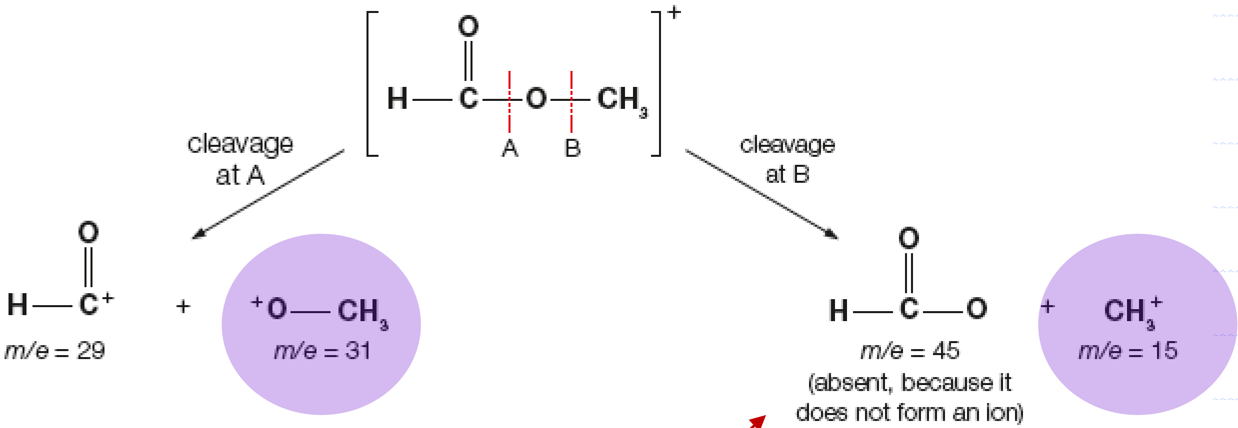

Figure 21.54 Ionic fragments formed from methyl methanoate

IB does not expect you to know where and to what degree compounds will cleave and be stable, but you should be able to problem solve a similar problem

no charge = no peak

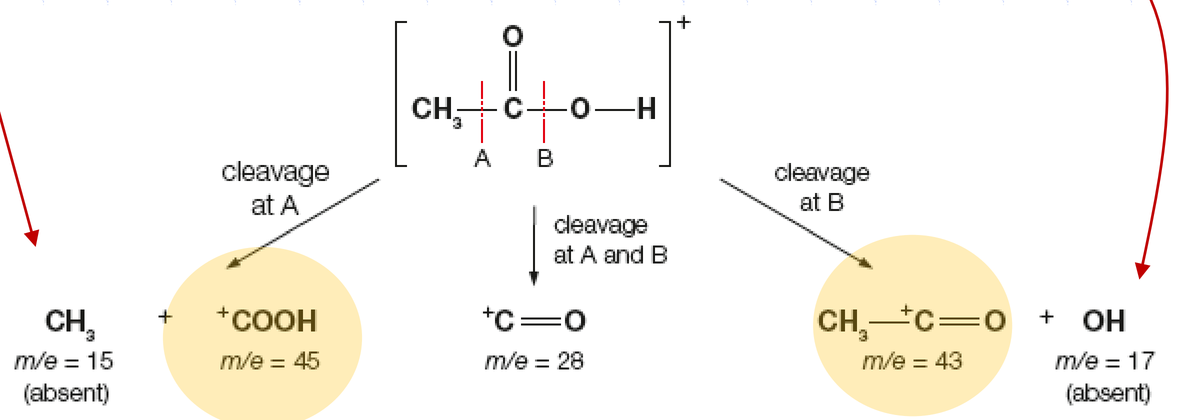

Figure 21.55 Ionic fragments formed from ethanoic acid

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Mass Spec of Isotopes

- Most elements have more than one naturally occurring, stable isotope.
- For Chlorine, ^{35}Cl and ^{37}Cl are both stable and in a 3:1 ratio in abundance respectively
  - For this reason, any compound containing Chlorine will give rise to “pairs” of peaks

H_3C-CH_2-Cl

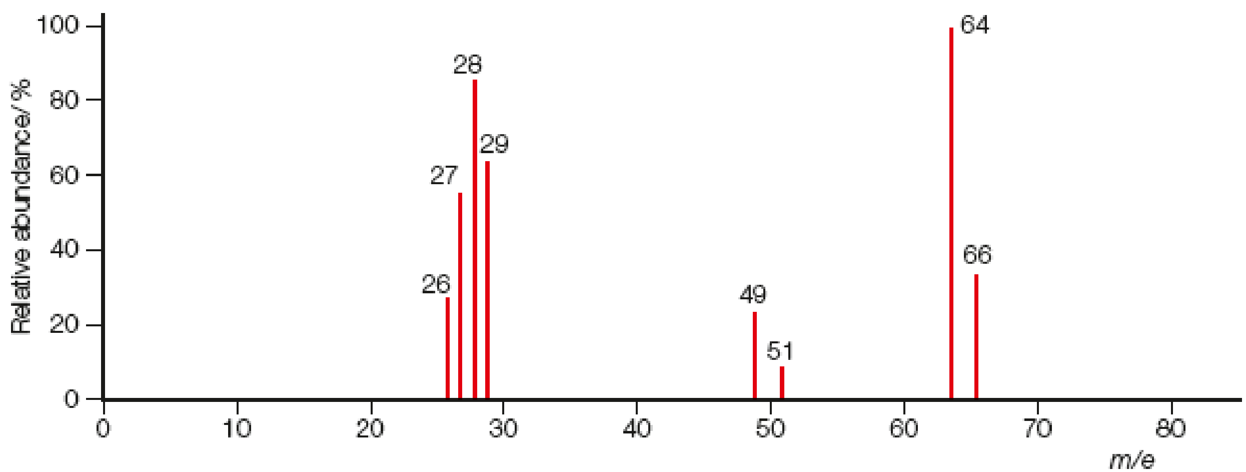

Figure 21.57 The mass spectrum of chloroethane